Molecular Symmetry and *Ab Initio* Calculations: IV. Symmetry-Matrix and Symmetry-Supermatrix in Calculations of Two-Electron Repulsion Integrals

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ABSTRACT

The product of two Gaussians having different centers is itself a one-center Gaussian, thus multicenter integrals with a Cartesian Gaussian basis can be reduced to one-center integrals. Recurrence relations for overlap integrals and electron repulsion integrals (ERIs) are derived at these centers. The calculations of overlap integrals and ERIs are carried out step by step from the highest symmetry case (one center) to required cases (different centers) by using the translation of Cartesian Gaussians. Full exploitation of symmetry in calculation processes can result in optimal use of these recurrence relations. Compared with the recently published algorithms, based on the recurrence relations derived by Obara and Saika [*J. Chem. Phys.*, **84**, 3963 (1986)], the floating point operations (FLOPs) for ERI calculations (having four different centers) can be reduced by a factor of ca. 2. A significant extra saving in calculations and storage can be obtained if atoms, linear, or planar molecules are discussed.

Introduction

In molecular quantum chemistry, calculation of electron repulsion integrals (ERIs) is one of the most important and time-consuming steps in the Hartree–Fock scheme. For efficient ERI calculations, the Cartesian Gaussian introduced by Boys[1] is often used. Recently, Obara and Saika[2] (OS) derived a recurrence relation which holds great potential. Head-Gordon and Pople[3] (HGP) derived another recurrence relation called the horizontal recurrence relation (HRR) from that of OS to reduce ERI calculations for the contracted basis. Lindh, Rys, and Liu[4] (LRL) and Hamilton and Schaefer[5] (HS) independently derived another kind of recurrence relation which can be used to simplify programming, especially for higher angular momentum cases in even-tempered, well-tempered,[6] or universal[7] basis sets. Combining the McMurchie–Davidson (MD) scheme[8] with the

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HGP algorithm,[3] the Prism method[9,10] developed by Gill, Head-Gordon, and Pople (GHP) can perform well for a wide range of classes of ERI. GHP's method[9] proved to be the best available method up to $(pp|pp)$ first-derivative cases. Several studies[11,12] have been published which further improve ERI calculations. However, the axis-switching method developed by Pople and Hehre[13] (PH) in 1970s is still the most efficient one for the highly contracted $(sp)^4$ shell case.

A primitive Cartesian Gaussian function at center $\mathbf{A} = [A_x\, A_y\, A_z]$ with exponent α_k is:

$$|\mathbf{a}\rangle \equiv \varphi_{ak}(\mathbf{r}) = x_A^{a_x} y_A^{a_y} z_A^{a_z} \exp(-\alpha_k \mathbf{r}_A^2) \tag{1}$$

where the angular momentum $\mathbf{a} = [a_x a_y a_z]$; $x_A = x - A_x$; $y_A = y - A_y$; $z_A = z - A_z$:

$$\mathbf{r}_A^2 = (\mathbf{r} - \mathbf{A})^2 = x_A^2 + y_A^2 + z_A^2$$

Primitive functions are often linearly combined to form a contracted Cartesian Gaussian function:

$$\phi_a(r) = \sum_{k=1}^{K} D_{ak} \varphi_{ak} \tag{2}$$

where D_{ak} is the contraction coefficient and K is the degree of contraction of the contracted function.

The essential step in the reduction of multicenter integrals is the application of the following theorem.[14] The product of two Gaussians having different centers A and B is itself a Gaussian with a center P somewhere on the line segment AB:

$$\exp(-\alpha r_A^2)\exp(-\beta r_B^2) = \exp\left(-\xi \overline{AB}^2\right)\exp(\zeta r_P^2) \tag{3}$$

where $\zeta = \alpha + \beta$; $\overline{AB} = A - B$:

$$P = \frac{\alpha A + \beta B}{\alpha + \beta} \tag{4}$$

$$\xi = \frac{\alpha\beta}{\alpha + \beta} \tag{5}$$

By using the equation:

$$\begin{aligned} &\frac{\partial}{\partial x}\int x_P^{p_x} \exp(-\zeta r_P^2) d\mathbf{r} \\ &\quad = \int \left(-2\zeta x_P^{p_x+1} + p_x x_P^{p_x-1}\right)\exp(-\zeta r_P^2) d\mathbf{r} \\ &\quad = 0 \end{aligned} \tag{6}$$

the overlap integral where the angular part at center P can be easily calculated:

$$\begin{aligned} \langle x_P^{p_x}\rangle &\equiv \int x_P^{p_x} \exp\left(-\xi\overline{AB}^2\right)\exp(-\zeta r_P^2) d\mathbf{r} \\ &= \frac{p_x - 1}{2\zeta}\langle x_P^{p_x-2}\rangle; \qquad p_x = \text{even} \end{aligned} \tag{7}$$

and $\langle x_P^{p_x}\rangle = 0$ if $p_x = $ odd.

To calculate $\langle x_A^{a_x}\rangle$, we only need to translate x_P to $x_A = x_P + \overline{PA}_x$, thus:

$$\langle x_A^{a_x+1}\rangle = \langle x_P\, x_A^{a_x}\rangle + \overline{PA}_x \langle x_A^{a_x}\rangle \tag{8}$$

where:

$$\langle x_P\, x_A^{a_x}\rangle = \frac{a_x}{2\zeta}\langle x_A^{a_x-1}\rangle \tag{9}$$

since

$$\frac{\partial}{\partial x}\langle x_A^{a_x}\rangle = -2\zeta\langle x_P\, x_A^{a_x}\rangle + a_x\langle x_A^{a_x-1}\rangle = 0.$$

Similarly, $\langle y_A^{a_y}\rangle$ and $\langle z_A^{a_z}\rangle$ can be calculated. Having finished $\langle \mathbf{a}_A\rangle \equiv \langle x_A^{a_x} y_A^{a_y} z_A^{a_z}\rangle$, we can do the contraction:

$$\begin{aligned} (\mathbf{a}_A) = \sum_k^K \sum_l^L D_{ak} D_{bl} \int x_A^{a_x} y_A^{a_y} z_A^{a_z} \exp(-\alpha_k r_A^2) \\ \times \exp(-\beta_l r_B^2) d\mathbf{r} \end{aligned} \tag{10}$$

Finally, we transform the angular parts to i_B; $i = x, y, z$, e.g.:

$$(i_B \mathbf{a}_A \mathbf{b}_B) = (i_A \mathbf{a}_A \mathbf{b}_B) + \overline{AB}_i (\mathbf{a}_A \mathbf{b}_B); \qquad i = x, y, z \tag{11}$$

This relation and eq. (8) are similar to the HRR in HGP.[3] However, in our case, this relation is derived directly, which can be used with not only the integral, but also any linear operator, such as the kinetic and nuclear attraction operators etc.

Even though the overlap matrix $[\langle \mathbf{a}|\mathbf{b}\rangle]$ has no symmetry, in the calculation processes these one-center overlap integrals $[\langle x_P^{p_x} y_P^{p_y} z_P^{p_z}\rangle]$, $[\langle x_A^{a_x} y_P^{p_y} z_P^{p_z}\rangle]$, $[\langle x_A^{a_x} y_A^{a_y} z_P^{p_z}\rangle]$, and $[\langle x_A^{a_x} y_A^{a_y} z_A^{a_z}\rangle]$ have permutation symmetry. Besides, the first three also have O_h, D_{4h}, and C_s symmetry, respectively. This method can be extended to calculate the electron repulsion integrals. Full exploitation of these local symmetry properties in the calculation processes can reduce greatly the matrix and ERI calculations. This is the reason why the axis-switching method of PH[13] is still the most efficient ERI calculation for the highly contracted $(sp)^4$ shell basis.

In this article, the concepts of symmetry-matrix and symmetry-supermatrix[15,16] will be used to reduce the ERI calculations.

Overlap Integral Calculations

The calculations of the two-center overlap integral $[\langle \mathbf{a}|\mathbf{b}\rangle]$ can be divided into five steps:

$$[\langle x_P^{p_x} y_P^{p_y} z_P^{p_z}\rangle] \rightarrow [\langle x_A^{a_x} y_P^{p_y} z_P^{p_z}\rangle] \rightarrow [\langle x_A^{a_x} y_A^{a_y} z_P^{p_z}\rangle] \rightarrow [\langle x_A^{a_z} y_A^{a_y} z_A^{a_z}\rangle] \rightarrow [\langle \mathbf{a}|\mathbf{b}\rangle]$$

It is easy to prove that the angular momentum, p_x, p_y, p_z, must be even, otherwise, the overlap integrals are zero. We will use an example $(spd)^2$ (the angular momentum of the basis $L \leq 2$) to demonstrate the calculation processes.

A. $[\langle x_P^{p_x} y_P^{p_y} z_P^{p_z}\rangle]$ CALCULATIONS

There are only four unique matrix elements in the overlap symmetry-matrix ($L \leq 2$). From eqs. (3)–(9):

$$\langle 1\rangle \equiv \int \exp(-\alpha r_A^2)\exp(-\beta r_B^2)\,d\mathbf{r} = \left(\frac{\pi}{\zeta}\right)^{3/2} \exp\left(-\xi \overline{AB}^2\right) \tag{12}$$

$$\langle z^2\rangle = \frac{1}{2\zeta}\langle 1\rangle \tag{13}$$

$$\langle y^2 z^2\rangle = \frac{1}{2\zeta}\langle z^2\rangle \tag{14}$$

$$\langle z^4\rangle = 3\langle y^2 z^2\rangle \tag{15}$$

Here the abbreviation $\langle x_P^{p_x} y_P^{p_y} z_P^{p_z}\rangle = \langle x^{p_x} y^{p_y} z^{p_z}\rangle$ is used. If one-center overlap integrals are calculated, then $A = B = P$, and the overlap matrix has O_h symmetry.

B. $[\langle x_A^{a_x} y_P^{p_y} z_P^{p_z}\rangle]$ CALCULATIONS

If we translate $P = [P_x P_y P_z]$ to $[A_z P_y P_z]$, we can get another six overlap symmetry-matrix elements:

$$\langle x|1\rangle = \overline{PA}_x\langle 1\rangle \tag{16}$$

$$\langle x^2|1\rangle = \overline{PA}_x\langle x|1\rangle + \langle z^2\rangle \tag{17}$$

since $\langle x_P^2\rangle = \langle z_P^2\rangle \equiv \langle z^2\rangle$:

$$\langle xz^2|1\rangle = \overline{PA}_x\langle z^2\rangle \tag{18}$$

$$\langle x^3|1\rangle = \overline{PA}_x\langle x^2|1\rangle + 2\langle xz^2|1\rangle \tag{19}$$

$$\langle x^2 z^2|1\rangle = \frac{1}{2\zeta}\langle x^2\rangle \tag{20}$$

$$\langle x^4|1\rangle = \overline{PA}_x\langle x^3|1\rangle + 3\langle x^2 z^2|1\rangle \tag{21}$$

Here the abbreviation $\langle x_A^{a_x}\rangle = \langle x^{a_x}|1\rangle$ is used. If A and B are located on the x-axis; i.e., $P_y = P_z = 0$, then the overlap matrix has D_{4h} symmetry, and only ten symmetry-matrix elements [eqs. (12)–(21)]. In the usual case, these ten elements can be transformed into $\frac{1}{6}5 \cdot 6 \cdot 7 = 35$ matrix elements by using the axis-switching method.

C. $[\langle x_A^{a_x} y_A^{a_y} z_P^{p_z}\rangle]$ CALCULATIONS

If A and B are located on the xy plane, i.e., $P_z = 0$, then the overlap matrix has C_s symmetry, and 22 symmetry-matrix elements. The number of symmetry-matrix elements for every angular momentum L can be determined by:

$$n(L) = \begin{cases} \left(\frac{L}{2} + 1\right)^2, & L\text{:even} \\ \frac{1}{4}(L+1)(L+3), & L\text{:odd} \end{cases} \tag{22}$$

If we change x to y in eqs. (16–21) and recalculate them, we can get a total of 12 symmetry-matrix elements. In addition to $\langle 1\rangle$, $\langle z^2\rangle$, and $\langle z^4\rangle$ in the "A" subsection the remaining seven symmetry-matrix elements are:

$$\langle xy|1\rangle = \overline{PA}_y\langle x|1\rangle \tag{23}$$

$$\langle x^2 y|1\rangle = \overline{PA}_y\langle xx|1\rangle \tag{24}$$

$$\langle x^2 y^2|1\rangle = \overline{PA}_y\langle x^2 y|1\rangle + \langle x^2 z^2|1\rangle \tag{25}$$

$$\langle x^3 y|1\rangle = \overline{PA}_y\langle x^3|1\rangle \tag{26}$$

If we exchange x and y in eqs (24) and (26), we can get a total of six symmetry-matrix elements. The last one, containing x, y, z components, is:

$$\langle xyz^2|1\rangle = \frac{1}{2\zeta}\langle xy|1\rangle \tag{27}$$

D. $[\langle x_A^{a_x} y_A^{a_y} z_A^{a_z}\rangle]$ CALCULATIONS

The number of symmetry-matrix elements for every angular momentum L in this case can be determined by:

$$n(L) = \tfrac{1}{2}(L+1)(L+2) \tag{28}$$

To obtain the 35 symmetry-matrix elements, we only need to calculate the integrals of one and two

components in the two previous subsections three times by using the operations in C_3. In this case, eqs. (18) and (20) are only intermediate integrals, thus four overlap integrals in subsection ''B'' can be obtained. Therefore, $(4 + 6) \cdot 3 = 30$ integrals can be obtained from subsections ''B'' and ''C''. In addition to $\langle 1 \rangle$, two three-component integrals are:

$$\langle xyz^2|1\rangle = \overline{PA}_x \overline{PA}_y \langle z^2|1\rangle \quad (29)$$

$$\langle xyz|1\rangle = \overline{PA}_z \langle yx|1\rangle \quad (30)$$

Permuting x, y, and z in eq. (29), we can get three overlap integrals.

E. $[\langle \mathbf{a}|\mathbf{b}\rangle]$ CALCULATIONS

Here we only discuss the $L = 4$ case. The abbreviation:

$$\langle x_A^{a_x} y_A^{a_y} z_A^{a_z} x_B^{b_x} y_B^{b_y} z_B^{b_z}\rangle = \langle x^{a_x} y^{a_y} z^{a_x}|x^{b_y} y^{b_y} z^{b_z}\rangle$$

will be used. There are four kinds of integrals in $[\langle x_A^{a_x} y_A^{a_y} z_A^{a_z}\rangle]$:

$$\langle x^4|1\rangle, \langle x^3 y|1\rangle, \langle x^2 y^2|1\rangle, \text{ and } \langle xyz^2|1\rangle$$

By using the operations in D_3, they can be transformed into 3, 6, 3, and 3 integrals, respectively. It totals up to 15 integrals at $A(L = 4)$, where each one can be transformed as:

$$\begin{aligned}
\langle x^4|1\rangle &\to \langle x^2|x^2\rangle \\
\langle x^3 y|1\rangle &\to \{\langle x^2|xy\rangle, \langle xy|x^2\rangle\} \\
\langle x^2 y^2|1\rangle &\to \{\langle x^2|y^2\rangle, \langle xy|xy\rangle, \langle y^2|x^2\rangle\} \\
\langle xyz^2|1\rangle &\to \{\langle xy|z^2\rangle, \langle xz|yz\rangle, \langle yz|xz\rangle, \langle z^2|xy\rangle\}
\end{aligned}$$

It totals up to 36 two-center integrals. These two-center integrals can be easily calculated; e.g., the three two-center integrals in the last transformation can be calculated as:

$$\langle xyz|z\rangle = \overline{AB}_z \langle xyz|1\rangle + \langle xyz^2|1\rangle \quad (31)$$

$$\langle xy|z^2\rangle = \overline{AB}_z \langle xy|z\rangle + \langle xyz|z\rangle \quad (32)$$

$$\langle xz|yz\rangle = \overline{AB}_y \langle xz|z\rangle + \langle xyz|z\rangle \quad (33)$$

$$\langle yz|xz\rangle = \overline{AB}_x \langle yz|z\rangle + \langle xyz|z\rangle \quad (34)$$

In eqs. (31)–(34), only eight floating point operations (FLOPs) instead of $3 \cdot 4 = 12$ are required to get three two-center integrals since they have the common intermediate integral $\langle xyz|z\rangle$. Transformations of 15 integrals at A $(L = 4)$ into 36 two-center integrals $[\langle \mathbf{a}|\mathbf{b}\rangle]$ require 114 FLOPs.

Table I illustrates the numbers of the symmetry-matrix elements of overlap matrices in various cases which depend on the segment $\overline{AB} \equiv \mathbf{R} \equiv [R_x R_y R_z]$.

ERI Calculations

A primitive ERI over four primitive Gaussians is the integral:

$$[\mathbf{a}_k \mathbf{b}_l|\mathbf{c}_m \mathbf{d}_n] = \iint \varphi_{ak}(\mathbf{r}_1)\varphi_{bl}(\mathbf{r}_1) \times r_{12}^{-1} \varphi_{cm}(\mathbf{r}_2)\varphi_{dn}(\mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2 \quad (35a)$$

The left-hand subscripts are usually neglected and it is denoted by $[\mathbf{ab}|\mathbf{cd}]$, and a contracted ERI:

$$(\mathbf{ab}|\mathbf{cd}) = \sum_k^K \sum_l^L \sum_m^M \sum_n^N D_{ak} D_{bl} D_{cm} D_{dn} [\mathbf{a}_k \mathbf{b}_l|\mathbf{c}_m \mathbf{d}_n] \quad (35b)$$

which we distinguish from a primitive ERI by the use of parentheses instead of brackets. To calculate $[\mathbf{ab}|\mathbf{cd}]$, we first calculate:

$$[\mathbf{p}|\mathbf{q}] = \iint x_{1P}^{p_x} y_{1P}^{p_y} z_{1P}^{p_z} \exp(-\zeta r_{1P}^2) \times r_{12}^{-1} x_{2Q}^{q_x} y_{2Q}^{q_y} z_{2Q}^{q_z} \times \exp\left(-\eta r_{2Q}^2\right) d\mathbf{r}_1\, d\mathbf{r}_2 \quad (36)$$

where ζ and P are as described in the previous section, $\eta = \gamma + \delta$ and;

$$Q = \frac{\gamma C + \delta D}{\gamma + \delta} \quad (37)$$

then use the method in the previous section to transform $[\mathbf{p}|\mathbf{q}]$ into $[\mathbf{ab}|\mathbf{cd}]$.

Because:

$$\exp(-\zeta r_P^2)\exp\left(-\eta r_Q^2\right) = \exp\left(-\rho \overline{PQ}^2\right)\exp(-\sigma r_W^2) \quad (38)$$

where $\sigma = \zeta + \eta$, $\overline{PQ} = P - Q$:

$$\rho = \frac{\zeta\eta}{\zeta + \eta} \quad (39)$$

$$W = \frac{\zeta P + \eta Q}{\zeta + \eta} \quad (40)$$

$$r^{-1} = \frac{2}{\pi^{1/2}} \int_0^\infty \exp(-r^2 u^2)\, du \quad (41)$$

and let $\mathbf{r} = \mathbf{r}_{12}$, $\mathbf{r}_2 = \mathbf{r}_1 - \mathbf{r}$, eq. (36) can be represented as:

$$[\mathbf{p}|\mathbf{q}] = \frac{2}{\pi^{1/2}} \iiint (\mathbf{p}_1\mathbf{q}_2)\exp\left(-\rho r_{PQ}^2\right) \times \exp(-\sigma r_{1W'}^2)\exp(-u^2 r^2)\, d\mathbf{r}_1\, d\mathbf{r}\, du \quad (42)$$

where $(\mathbf{p}_1\mathbf{q}_2)$ represents the angular parts in eq. (36), $r_{PQ}^2 = (\mathbf{r} - \overline{PQ})^2$:

$$W' = W + \frac{\rho}{\zeta}\mathbf{r} \quad (43)$$

By using the following equations:

$$W'_x - P_x = \frac{\rho}{\zeta}x + \overline{WP}_x = \frac{\rho}{\zeta}\left(x - \overline{PQ}_x\right) \quad (44)$$

$$V = \frac{\rho\overline{PQ}}{\rho + u^2} \quad (45)$$

$$\frac{\rho}{\zeta}\left(V_x - \overline{PQ}_x\right) = \overline{WP}_x\left(\frac{u^2}{\rho + u_2}\right) \quad (46)$$

$$[\mathbf{p}|\mathbf{q}]^m = \frac{2}{\pi^{1/2}} \iiint (\mathbf{p}_1\mathbf{q}_2)\exp\left(-\rho r_{PQ}^2\right) \times \exp(-\sigma r_{1W'}^2)\exp(-u^2 r^2) \times \left(\frac{u^2}{\rho + u^2}\right)^m d\mathbf{r}_1\, d\mathbf{r}\, du \quad (47)$$

we get:

$$[\, x_{1P}\mathbf{p}|\mathbf{q}]^m = \overline{WP}_x[\mathbf{p}|\mathbf{q}]^{m+1} + [\, x_{1W}\mathbf{p}|\mathbf{q}]^m \quad (48)$$

where:

$$[\, x_{1W}\mathbf{p}|\mathbf{q}]^m = \frac{p_x}{2\zeta}\left\{[\mathbf{p} - \mathbf{1}_x|\mathbf{q}]^m - \frac{\rho}{\zeta}[\mathbf{p} - \mathbf{1}_x|\mathbf{q}]^{m+1}\right\} + \frac{q_x}{2\sigma}[\mathbf{p}|\mathbf{q} - \mathbf{1}_x]^{m+1} \quad (49)$$

and the angular momentum of $\mathbf{p} - \mathbf{1}_x$ $(\mathbf{q} - \mathbf{1}_x)$ is equal to $[\, p_x - 1 p_y p_z]$ $([\, q_x - 1 q_y q_z])$. Therefore, any two electron integral $[\mathbf{p}|\mathbf{q}]$ can be transformed from Gaussian $s(\sigma = 0)$ function integrals

$$\left[1_P|1_Q\right]^m = \frac{2}{\pi^{1/2}} \iiint \exp\left(-\rho r_{PQ}^2\right)\exp(\sigma r_{1W'}^2) \times \exp(-u^2 r^2)\left(\frac{u^2}{\rho + u^2}\right)^m d\mathbf{r}_1\, d\mathbf{r}\, du$$

by using eq. (48).

It should be pointed out that the translation $x_{1P} \rightarrow x_{1W} + \overline{WP}_x$ in eq. (48) is different from the HRR in the ''Overlap Integrals Calculation'' section and HGP[3]. Here, along with a change of angular parts, the Gaussian parts in $[\, x_{1W}\mathbf{p}|\mathbf{q}]$ are also changed to $\exp(-\zeta r_{1W}^2)$.

The ERI calculations can be divided into the following steps:

$$\begin{aligned}[\mathbf{w}|\mathbf{w}] &\rightarrow \left[P_x W_y W_z|Q_x W_y W_z\right] \\ &\rightarrow \left[P_x Q_y W_z|P_x Q_y W_z\right] \\ &\rightarrow \left[P_x P_y P_z|Q_x Q_y Q_z\right] \\ &\rightarrow \left[P_x P_y P_z|C_x C_y C_z\right) \rightarrow \left(A_x A_y A_z|C_x C_y C_z\right) \\ &\rightarrow (\mathbf{ab}|\mathbf{cd})\end{aligned}$$

Here the centers of Cartesian Gaussian functions are presented. We first calculate the ERIs at W,

TABLE I.
The Numbers of Symmetry-Matrix Elements of Overlap Matrices in Various Cases.

	One-Center Overlap Matrix $[R_x R_y R_z]$				
L	$[000](O_h)$	$[R_x 00](D_{4h})$	$[R_x R_y 0](C_s)$	$[R_x R_y R_z]$	$[\langle \mathbf{a}|\mathbf{b}\rangle]$
0	1	1	1	1	1
1	1	2	4	6	9
2	2	4	9	15	36
3	3	6	16	28	100
4	4	9	25	45	225
5	5	12	36	66	441
6	7	16	49	91	784
7	8	20	64	120	1296
8	10	25	81	153	2025

$\overline{AB} \equiv \mathbf{R} \equiv [R_x R_y R_z]$.

then transform them step by step into P and Q by using eqs. (48) and (49). The last three steps are transformed by using the HRR eq. (11). These are the same with the transformation described in subsection ''E'' of the previous section. Only the $(sp)^4$ shell ERI calculations are described in this section.

A. [w|w] CALCULATIONS

If $P = Q = W$, then only one-center ERIs [**w**|**w**] need to be calculated. These ERIs have O_h symmetry:

$$[\,zz|1]^m = \frac{1}{2\zeta}\left\{[1|1]^m - \frac{\rho}{\zeta}[1|1]^{m+1}\right\}; \qquad m = 0, 1, 2 \tag{50}$$

$$[\,z|z]^m = \frac{1}{2\sigma}[1|1]^{m+1}; \qquad m = 0, 1 \tag{51}$$

$$2[\,yz|yz] = \frac{1}{\sigma}[\,z|z]^1 \tag{52}$$

$$[\,zz|yy] = \frac{1}{2\eta}\left\{[\,zz|1] - \frac{\rho}{\eta}[\,zz|1]^1\right\} \tag{53}$$

$$[\,zz|zz] = [\,zz|yy] + 2[\,yz|yz] \tag{54}$$

In eq. (50), if $\zeta \neq \eta$, then $[1|zz]$ can be calculated by exchanging ζ and η. Only 16 FLOPs need to calculate [**w**|**w**] except [1|1].

B. $[P_xW_yW_z|Q_xW_yW_z]$ CALCULATIONS

If P and Q are located on the x-axis, $[P_zW_yW_z|Q_xW_yW_z]$ need to be calculated. These ERIs have D_{4h} symmetry.

$$[\,x|1]^m = \overline{WP}_x[1|1]^{m+1}; \qquad m = 0, 1, 2, 3 \tag{55}$$

$$[\,xx|1]^m = \overline{WP}_x[\,x|1]^{m+1} + [\,zz|1]^m; \qquad m = 0, 1, 2 \tag{56}$$

$$[\,x|x]^m = \overline{WQ}_x[\,x|1]^{m+1} + [\,z|z]^m; \qquad m = 0, 1 \tag{57}$$

$$2[\,xz|z]^m = 2\overline{WP}_x[\,z|z]^{m+1}; \qquad m = 0, 1 \tag{58}$$

$$[\,xx|x]^m = \overline{WQ}_x[\,xx|1]^{m+1} + 2[\,xz|z]^m; \qquad m = 0, 1 \tag{59}$$

$$2[\,xz|xz] = \frac{1}{\sigma}[\,x|x]^1 \tag{60}$$

$$[\,xx|zz] = \frac{1}{2\eta}\left\{[\,xx|1] - \frac{\rho}{\eta}[\,xx|1]^1\right\} \tag{61}$$

$$[\,xx|xx] = \overline{WQ}_x[\,xx|x]^1 + [\,xx|zz] + 2[\,xz|xz] \tag{62}$$

$$[\,x|zz] = \overline{WP}_x[1|zz]^1 \tag{63}$$

if $\zeta \neq \eta$, eqs. (55), (56), (58), (59), (61), and (63) need to be recalculated by exchanging ζ and η. To calculate $[xx|xx]$, all above eqs. (55)–(61) are needed. 19 + 41 = 60 FLOPs are needed to calculate $[P_xW_yW_z|Q_xW_yW_z]$.

C. $[P_xP_yW_z|Q_xQ_yW_z]$ CALCULATIONS

If P and Q are located on the xy plane, or if a local coordinate system in which P, C, and D are located on the xy plane is established, then we need to calculate $[P_xP_yW_z|Q_xQ_yW_z]$. These ERIs have C_s symmetry.

In addition, the calculations in eqs. (55)–(63) need to be recalculated by changing x to y. Besides, the ERIs containing (x, y) and (x, y, z) need to be calculated:

$$[\,y|x]_2 = \overline{WQ}_x[\,y|1]^1 \tag{64}$$

$$[\,xy|1]_2 = \overline{WP}_x[\,y|1]^1 \tag{65}$$

$$[\,yy|x]_4^m = \overline{WQ}_x[\,yy|1]^{m+1}; \qquad m = 0, 1 \tag{66}$$

$$[\,xy|y]_4^m = \overline{WP}_x[\,y|y]^{m+1}; \qquad m = 0, 1 \tag{67}$$

$$[\,yy|xy]_4 = \overline{WQ}_x[\,yy|y]^1 \tag{68}$$

$$[\,xy|xy]_1 = \overline{WQ}_x[\,xy|y]^1 + [\,yz|yz] \tag{69}$$

$$[\,yy|xx]_2 = \overline{WQ}_x[\,yy|x]^1 + [\,yy|zz] \tag{70}$$

Here the subscript means the calculation times of the equation if (x, y) and (ζ, η) are exchanged. A total of 25 FLOPs are needed to calculate eqs. (64)–(70):

$$[\,xy|zz]_2 = \overline{WP}_x\overline{WP}_y[1|zz]^2 \tag{71}$$

$$[\,xz|yz]_2 = \overline{WP}_x\overline{WQ}_y[\,z|z]^2 \tag{72}$$

Therefore, a total of 22 + 82 + 33 = 137 FLOPs are needed to calculate $[P_xP_yW_z|Q_xQ_yW_z]$.

D. $[P_xP_yP_z|Q_xQ_yQ_z]$ CALCULATIONS

To calculate $[P_xP_yP_z|Q_xQ_yQ_z]$, the equations in the two previous subsections must be calculated three times by using operations in C_3 symmetry. Besides:

$$[\,xy|z]_6 = \overline{WP}_x\overline{WP}_y[1|z]^2 \tag{73}$$

TABLE II.
FLOP Counts for $(sp)^4$ ERI Calculations.

					This Work		
$(sp)^4$	PH[13]	HGP[3]	GHP[9]	LRL[4]	O_h	D_{4h}	C_s	No Sym.
μ	220	1400	450	851	16	72	213	474
ν	2300	30	1300	30	0	44	172	368
λ	4000	800	1700	800	0	40	192	468

The FLOP counts $N = \mu K^4 + \nu K^2 + \lambda K^0$, where K is the degree of contraction.

Therefore, a total of $21 + 3 \cdot 36 + 3 \cdot 33 + 12 = 240$ FLOPs are needed.

E. (*ab*|*cd*) CALCULATIONS

(ab|cd) calculations from $[P_x P_y P_z|Q_x Q_y Q_z]$ are divided into three steps:

$$\begin{aligned}\left[P_x P_y P_z|Q_x Q_y Q_z\right] &\rightarrow \left[P_x P_y P_z|C_x C_y C_z\right) \\ &\rightarrow \left(A_x A_y A_z|C_x C_y C_z\right) \\ &\rightarrow (\mathbf{ab}|\mathbf{cd})\end{aligned}$$

where |) or (| mean the contracted ERIs.

The FLOP counts for $(sp)^4$ ERI calculations:

$$N = \mu K^4 + \nu K^2 + \lambda K^0 \qquad (74)$$

where, for simplicity, each of the four shells involved is assumed to have the same degree of contraction K. The FLOP counts for the first step are proportional to the degree of contraction K^4. Having finished the $[P_x P_y P_z|C_x C_y C_z]$, we can do the contraction $[P_x P_y P_z|C_x C_y C_z)$. Therefore, the FLOP counts of the next step $(A_x A_y A_z|C_x C_y C_z)$ are proportional to K^2, and those of the last step are proportional to K^0.

Table II illustrates the FLOP counts for $(sp)^4$ ERI calculations. In our work, the FLOP count ($\mu = 474$) is about 56% of that in LRL method.[4] This is because these transformations ($P_x P_y P_x \rightarrow A_x A_y A_z$) are transformed from the inner loop (K^4) to the outer loop (K^2). Compared with the GHP method,[9] this value ($\mu = 474$) is near to GHP's ($\mu = 450$), but ν and λ in our case are much smaller. If ERIs **(ab|cd)** have some symmetry, the FLOP counts can be greatly reduced. If planar molecules are included, the ERIs at least have C_s symmetry, and the FLOP count is $\mu = 213$ which is similar to PH's.[13] Therefore, if two local coordinate systems (where xy planes are PCD and ABC, respectively) are established, then a more efficient axis-switching method can be developed since the FLOP count is $\mu = 175$ if the x axis is parallel to CD. A reduction factor can reach $220/175 = 1.27$.

Conclusion and Discussion

The product of two Gaussians having different centers is itself a one-center Gaussian, thus multicenter integrals with a Cartesian Gaussian basis

TABLE III.
Elements of Symmetry Basis up to Angular Momentum $L \leq 8$.

L	$n(L) = \frac{1}{2}(L+1)(L+2)$	Symmetry Basis Elements for Angular Momentum L
0	1	1
1	3	$3z$
2	6	$3yz, 3z^2$
3	10	$xyz, 6yz^2, 3z^3$
4	15	$3xyz^2, 3y^2z^2, 6yz^3, 3z^4$
5	21	$3xy^2z^2, 3xyz^3, 6y^2z^3, 6yz^4, 3z^5$
6	28	$x^2y^2z^2, 6xy^2z^3, 3xyz^4, 3y^3z^3, 6y^2z^4, 6yz^5, 3z^6$
7	36	$3x^2y^2z^3, 3xy^3z^3, 6xy^2z^4, 3xyz^5, 6y^3z^4, 6y^2z^5, 6yz^6, 3z^7$
8	45	$3x^2y^3z^3, 3x^2y^2z^4, 6xy^3z^4, 6xy^2z^5, 3xyz^6, 3y^4z^4, 6y^3z^5, 6y^2z^6, 6yz^7, z^8$

can be reduced to one-center integrals. In the overlap matrix calculations, these one-center overlap integrals can be easily calculated, then these integrals can be transformed by the following steps:

$$\langle \mathbf{p} \rangle (O_h) \rightarrow \langle A_x P_y P_z \rangle (D_{4h}) \rightarrow \langle A_x A_y P_z \rangle (C_s) \rightarrow \langle A_x A_y A_z \rangle \rightarrow \langle \mathbf{a} | \mathbf{b} \rangle$$

The numbers of symmetry-matrix elements of these overlap matrices are presented in Table I. In this article, the calculations of the $(spd)^2$ overlap matrix are only described, but can be easily extended to higher angular momentum cases. The symmetry-matrix elements of $[\langle \mathbf{p} \rangle]$ are similar to the elements of the symmetry-basis (composed of nonequivalent basis functions),[15–17] because the angular momentum p_x, p_y, p_z of $[\langle \mathbf{p} \rangle]$ must be even, i.e., twice the angular momentum of basis functions. Table III illustrates the elements of the symmetry basis up to $L \leq 8$. These elements are useful to calculate $(spdfg)^4$ ERIs. In the calculation processes, not only the point symmetry but the permutation symmetry can be used. For example, the number of one-center overlap integrals is only 20% that of two-center's for $(g)^2$ overlap matrix (Table I). In the last step, we often transform these integrals into spherical harmonics, some equivalent basis functions,[17] or the general contraction basis[18,19] to further reduce the storage and avoid instability caused by the dependency of basis functions. Finally, an overlap symmetry-matrix[15–17] will be formed.

From the previous section we can find that the recurrence relations, (eqs. (48) and (49) for two-center (P and Q) ERIs only have four terms. They can be reduced to three terms if ERIs are calculated at W, and even further reduced to two or one term if the angular momentum, q_x or p_x is equal to zero. Therefore, full exploitation of symmetry will permit optimal use of these recurrence relations for ERI calculations.

In the last step of the ERI calculations, we should transform ERIs first to $(A_x A_y A_z|\mathbf{cd})$, and then to $(\mathbf{ab}|\mathbf{cd})$. By using this method, not only calculations but also memory can be reduced. The original ERIs can be transformed into new ERIs, and only extra ERIs need new memory. For the $(p)^4$ case, the FLOP count $\lambda = 18(6 + 9) = 270$ instead of $4 \cdot 81 = 324$.[3] A reduction factor $6/5 = 1.2$ can be obtained. For $(d)^4$, $(f)^4$, and $(g)^4$, the FLOP counts λ are 5814, 47,616, and 280,260, respectively. Compared with the latest results (11,300, 111,012, and 663, 780),[12] the reduction factors can reach 1.94, 2.33, and 2.39, respectively.

The method based on the piecewise transformations is very important in the final formation of contracted ERIs $(\phi_a \phi_b|\phi_c \phi_d)$ from primitive ERIs $[\varphi_a \varphi_a|\varphi_c \varphi_c]$. In programming, the formation of contracted ERIs is divided into the following steps:

$$[\varphi_a \varphi_a|\varphi_c \varphi_c] \rightarrow [\varphi_a \varphi_a|\varphi_c \phi_d) \rightarrow [\varphi_a \varphi_a|\phi_c \phi_d) \rightarrow (\varphi_a \phi_b|\phi_c \phi_d) \rightarrow (\phi_a \phi_b|\phi_c \phi_d)$$

where φ is the primitive basis and ϕ is the contracted basis which can be spherical harmonic, equivalent basis,[17] or the general contracted basis,[18,19] then the calculations and storage of ERIs can be reduced simultaneously. Finally, these contracted ERIs can be transformed into symmetry-supermatrix[15,16] for further application in Hartree–Fock or post-Hartree–Fock methods.

In our programming, the calculations of overlap integrals and ERIs are carried out step by step from the highest symmetry case to required cases. These high symmetry cases will be met in the real calculation, e.g., in some two-electron integrals $A = B$, $C = D$, or they are located on coordinate axes or planes, then the corresponding transformations can be skipped automatically. Therefore, a significant extra saving in calculations and storage can be obtained if atoms or linear or planar molecules are discussed.

The concepts of symmetry-matrix and symmetry-supermatrix[15–17] will cause significant changes in programming. The symmetry-supermatrix can be used to discuss the electron correlation if natural spin orbitals[20] are used. We are now developing programs for electron correlation, including relativistic effects by using even-tempered, well-tempered,[6] or universal[7] basis sets.

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